

# INVESTIGATION OF LITHIUM DIFFUSION IN OXIDE FILM ELECTRODES BY OPTICAL AND ELECTROCHEMICAL PITT

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## Abstract

Transition metal oxide thin films are of considerable technological interest as electrodic materials for electrochemical devices (lithium-ion microbatteries, electrochromic devices, displays etc.). For such electrochemical applications these materials are considered promising as, due to their suitable structure, they fulfill some basic requirements as high ion-charge capacity and fast charge transfer at the electrode/electrolyte interface and diffusion through the film. In particular quantitative knowledge of transport kinetics parameters in thin solid films is of great importance as the response time of the electrochemical device is determined by the rate of charge and diffusion processes.

The subject of the present paper deals with the study of solid-state electrochemical kinetics of Li-ion intercalation into RF sputtered WO<sub>3</sub> and Ni/V mixed oxides films using Potentiostatic Intermittent Titration Technique (PITT).

In the case of the electrochromic[1] RF sputtered amorphous WO<sub>3</sub> films 2 different approaches of PITT were used: the diffusion coefficient D<sub>Li</sub> of Li<sup>+</sup> in the oxide, that quantitatively describes the Li<sup>+</sup> diffusion process inside the electrode, was evaluated both by the theoretical treatment of PITT data already used by Levi et al.[2] but also by a new and original method which consists in the analysis of the optical behavior during the potential step. This method is equivalent, in the time domain, to the color impedance methods developed for the frequency domain [3, 4, 5]. According to the method in[2], PITT elaboration data is based on the analysis of the current-time curves by plotting  $It^{1/2}$  vs  $\log t$ . By integration of the Cottrell equation we have found that D<sub>Li</sub> can also be calculated by the analysis of the following expression:

$$Q(t)t^{-1/2} = 2 \frac{D_{Li}^{1/2} \Delta Q}{l\pi^{1/2}} \quad (1)$$

where  $Q(t)t^{-1/2}$  is the value of the plateau in the  $Q(t)t^{-1/2}$  vs  $\log t$  plot, representing the diffusion-controlled region,  $\Delta Q$  is the charge injected during the pulse and  $l$  is the film thickness.

We could apply equation (1) substituting  $Q(t)$  with the optical density  $OD(t)$  if the hypothesis that there is a linear relation between the charge inserted  $Q(t)$  and  $OD(t)$  holds. Diffusion coefficients can be calculated as before from the  $OD t^{-1/2}$  vs  $\log t$  plot

We have demonstrated that the results obtained with the two types of techniques are consistent with the above hypothesis.

We also analyzed the kinetics of Li<sup>+</sup> insertion in Ni/V oxides [6] that can be used as transparent counterelectrodes in electrochromic devices (ECDs). In that case the films are optically passive during the intercalation process so they do not change color but keep a high transmittance in both inserted/deinserted states. This property did not allow us to perform optical PITT on such films so we only used the classical electrochemical PITT approach. The plot of D<sub>Li</sub> vs inserted charge ( $Q_{ins}$ ) showed an initial increase of D<sub>Li</sub> probably related to a change in the electronic properties and upon further intercalation a slow down of the diffusion rate due to a decrease in the number of occupable sites in the host structure.

Concerning the electrochemical applications, it is important to point out that, although Ni/V films were much thinner (110 nm) than WO<sub>3</sub> ones (1000 nm), the Li<sup>+</sup> diffusion time  $t_D$  was longer. The insertion of 30 mC cm<sup>-2</sup>, the minimal charge required to have good electrochromic efficiency, resulted in a  $t_D$  value of 550s for Ni/V oxide films and of 250s for WO<sub>3</sub>. This result implies that in a WO<sub>3</sub>-based ECD, Ni/V oxides counterelectrodes would be the kinetically limiting element.

**Keywords:** diffusion, Li injection, PITT, thin films.

## References

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